Effect of Oxygen and Diborane Gas Ratio on P-type Amorphous Silicon Oxide films and Its Application to Amorphous Silicon Solar Cells

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We reported diborane (B_2H_6) doped wide bandgap hydrogenated amorphous silicon oxide (p-type a-SiOx:H) films prepared by using silane (SiH_4) hydrogen (H_2) and nitrous oxide (N_2O) in a radio frequency (RF) plasma enhanced chemical vapor deposition (PECVD) system. We improved the E_{opt} and conductivity of p-type a-SiOx:H films with various N_2O and B_2H_6 ratios and applied those films in regards to the a-Si thin film solar cells. For the single layer p-type a-SiOx:H films, we achieved an optical band gap energy (E_{opt}) of 1.91 and 1.99 eV, electrical conductivity of approximately 10^{-7} S/cm and activation energy (E_a) of 0.57 to 0.52 eV with various N_2O and B_2H_6 ratios. We applied those films for the a-Si thin film solar cell and the current-voltage characteristics are as given as: V_{oc} = 853 and 842 mV, J_{sc} = 13.87 and 15.13 mA/cm^2. FF = 0.645 and 0.656 and η = 7.54 and 8.36% with B_2H_6 ratios of 0.5 and 1% respectively.

Keywords: Activation energy, Silane gas, a-Si thin film solar cell, Diborane doped amorphous silicon oxide films, PECVD

1. INTRODUCTION

In a p-i-n type thin film amorphous silicon (a-Si) solar cell, optoelectronic properties of the window layer are of significant importance. For high performance, the p-layer of the solar cell should have a high optical bandgap to minimize optical absorption, high dark conductivity and photoconductivity to reduce series resistance, low activation energy to obtain higher open circuit voltage (V_{oc}), and a narrow valence band tail in order to obtain higher short circuit current density (J_{sc}). As the wide opti-cal gap window layer ensures less light lost in absorption at the p-layer, higher J_{sc} can be achieved [1].

Boron doped hydrogenated amorphous silicon carbide (p-type a-SiC:H) films have been mostly used for this purpose. However, the incorporation of carbon in the p-type a-SiC:H films give rise to a void structure, and caused an increased defect density. In contrast, p-type a-SiO$_x$:H films have a lower defect density, Urbach energy and comparatively high doping efficiency [2]. Therefore, the p-type a-SiO$_x$:H films provide a wide bandgap and higher photoconductivity compared to other wide bandgap hydrogenated amorphous silicon materials, which could be useful as a window layer for the solar cells [1,3-4].

In this paper, we prepared a-SiO$_x$:H films by varying N_2O gas as a p-layer window for a-Si solar cells. We also reported the electrical and optical properties of silicon oxide for different N_2O and B_2H_6 gas ratios as well as current-voltage characteristics for a-Si

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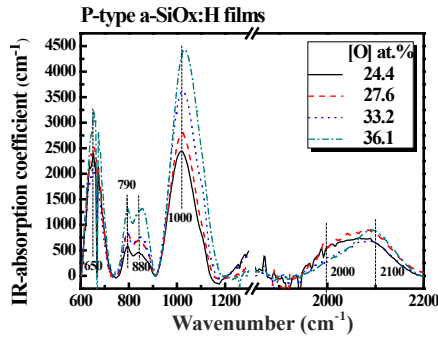⚠ Trans. Electr. Electron. Mater. 13(4) 192 (2012): J. Park *et al.*

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Fig. 1. The absorption coefficient from 600 to 2,200 cm^{-1} attained by FT-IR spectra of p-type a-SiO$_x$:B -SiO$_x$:H films with different oxygen concentration.
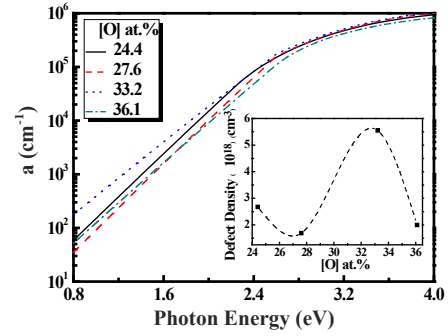

Fig. 2. The absorption coefficient measured by SE for p-type a-SiO$_x$:H films with different oxygen concentrations as a function of photon energy. The inset shows defect density, which can be deduced from the integrated absorption from 0.8 to 1.6 eV around the Urbach edge contribution.

solar cells with p-type a-SiO$_x$:H films as a window layer.

2. EXPERIMENTAL

P-type a-SiO$_x$:H films were deposited by the RF PECVD technique on a glass (Eagle 2000 glass, size 5 × 5 cm^2, 1 mm-thick) and Si wafer with (100) orientation as substrates. The glass substrates were ultrasonically cleaned by dipping in acetone, isopropyl alcohol, and de-ionized water for 5 min. The 0.2 μm film thickness was fixed for each sample at a substrate temperature (T$_s$) of 175℃ through the glow discharge decomposition of silane (SiH$_4$), hydrogen (H$_2$), nitrous oxide (N$_2$O 90% diluted in He), and diborane (B$_2$H$_6$ 99% diluted in H$_2$) gas mixtures, with gas flow rates of SiH$_4$=10 sccm, N$_2$O(+He)=3(+27), 5 sccm, B$_2$H$_6$(+H$_2$)=0.05(+4.95), 0.1 (+9.90) sccm, H$_2$=95, and 90 sccm. The RF power density of 50 mW/cm^2, pressure of 0.2 Torr and an electrode separation of 4.0 cm was used for the whole process.

The Fourier transform infrared spectroscopic (FTIR) (Prestige-21 spectrometer, Shimadzu, in 7,800 ~ 350 cm^{-1}) system was used to estimate the concentration of oxygen (C(O) at.%) within the film measurements on Si samples. The asymmetric stretching vibration of oxygen in the Si-O-Si bond was detected at a wave number of approximately 1,000 cm^{-1} and was used to calculate the oxygen content with the help of a calibration constant from reference [30]. The spectroscopic ellipsometry (SE), (VASE®, J.A. Woollam, 240 nm < λ < 1,700 nm) was used in order to measure the sample thickness (d), refractive index (n) and optical absorption coefficient α at an incident angle of 65° in the spectral wavelength range of 240 nm to 1,700 nm. The electrical characteristics (dark conductivity activation energy (E$_a$)) were studied by using programmable (Keithley 617 electrometer) at 25 to 125℃ temperature range.

We fabricated the a-Si solar cell with p-type a-SiO$_x$:H window layer while the i and n-type (1% phosphine, PH$_3$, doped) layers are a-Si:H based. The quantum efficiency (QE) of a-Si solar cell was measured by the QEX7 system (PV measurement Inc.QEX7).

3. RESULTS AND DICUSSION

Figure 1 shows the absorption coefficient between 600 and 2,200 cm^{-1} attained by FT-IR spectra of p-type a-SiO$_x$:H films with different oxygen contents. By neglecting reflectance, the absorption coefficient α is directly defined from the relation [5].

$$\alpha = [2.303 \log(1/T)]/d \qquad (1)$$

where d is film thickness in centimeters and T is the transmittance by measuring the FT-IR spectra. The spectra exhibits absorption peaks corresponding to an Si-O-Si rocking at 650 cm^{-1}, overlap of a local bond configuration with mixed bending and stretching character for oxygen and hydrogen atoms (H-Si(Si$_2$O)) at 790 cm^{-1}, HSi-O$_3$ bending at 880 cm^{-1}, Si-O-Si stretching at 1,000 cm^{-1}, Si-H stretching at 2,000 cm^{-1}, and Si-H$_2$ stretching at 2,100 cm^{-1}[10-14]. The integrated absorption band centered at around 1,000 cm^{-1} mainly represents oxygen content by the following relation [6].

$$C(O) = A(O)I(940 - 1080) \qquad (2)$$

where C(O) is the oxygen concentration (units of at.%), A(O) = 0.156 at.%/eV cm^{-1} and I(940-1080) is the integrated absorption. Considering this mathematical relation, the oxygen content depends critically on N$_2$O and B$_2$H$_6$ gases ratio. With increasing N$_2$O gas ratio (30 and 50%) and decreasing B$_2$H$_6$ gas ratio (0.5 and 1%), the oxygen content increased from 24.4 to 36.1 at.%. The peak position was shown to shift slightly to higher wave numbers with increasing oxygen content. The presence of more electronegative neighboring atoms shifts the peak toward higher wave numbers and this shift is due to the reduction of the bond length caused by the transfer of valence electrons to more electronegative neighboring atoms [6]. The properties of p-type a-SiO$_x$:H films such as I(940-1080), oxygen content, E$_{opt}$ and refractive index are summarized in Table 1.

In Fig. 2 the absorption coefficient (α) measured by spectroscopic ellipsometry (SE) of p-type a-SiO$_x$:H films for oxygen content between 24.4 and 36.1 at.% displayed. The absorption area is divided into three regions - the defect region (0.8~1.6 eV), the band tail region (1.6~2.0 eV) and the band to band absorption region (2.0 eV~). In regards to the defect region, absorption occurred by defect states located in the middle of the gap for the defect region [7]. We can deduce defect density (N$_D$) from the integrated absorption in the defect region by using the below mathematical expression.

$$N_D = \frac{cnm_e}{2\pi^2\hbar^2}\left[\frac{(1+2n^2)}{9n^2e^2 f_{of}}\right]\int_0^{E_{max}}\alpha_{mean}(E)\,d(E)$$

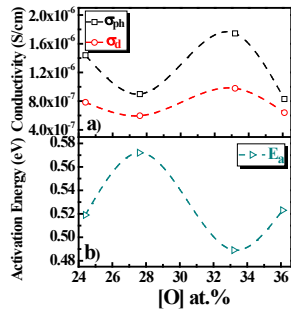$$= 7.9\times10^{15}\int_0^{E_{max}}\alpha_{mean}(E)\,d(E) \qquad (3)$$

Fig. 3. Room-temperature dark and photo conductivities (a) and activation energies (b) of p-type a-SiO$_x$:B -SiO$_x$:H films as a function of oxygen content.
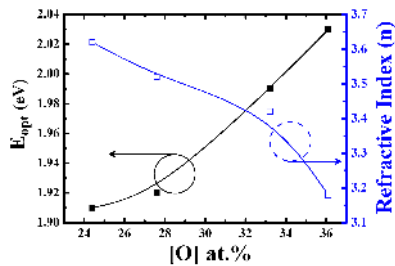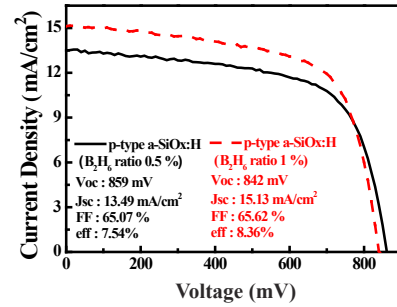

Fig. 5. Performance of solar cells with p-type a-SiO$_x$:H layers with different B$_2$H$_6$ ratios. Amorphous silicon solar cell I-V characteristic measured at room temperature under the AM 1.5 G condition.

Fig. 4. Variation in optical bandgap E$_g$ and refractive index n (taken at 632 nm wavelength) for p-type a-SiO$_x$:B -SiO$_x$:H films as a function of oxygen content.
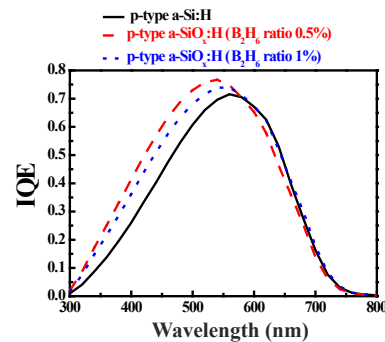

Fig. 6. Spectral response of solar cells with different window materials. Each condition of window materials is ■ - (p-tye a-Si:H/E$_{opt}$ = 1.75 eV), ● - (p-type a-SiO$_x$:H/E$_{opt}$ = 1.94 eV) and ▲ - (p-type a-SiO$_x$:H/E$_{opt}$ = 1.91 eV).

where N$_D$ is the defect density, α$_{means}$ is the measured defect absorption, c is the velocity of light, n is the refractive index, m$_e$ is the electron mass and E$_{max}$, of approximately 1.6 eV, after subtracting the Urbach edge contribution. For E$_{opt}$ = 1.91-2.03 eV, the N$_D$ increased from 1.91×10^{18} cm^{-3} to 5.55×10^{18} cm^{-3} (see inset of Fig. 2). In general, N$_D$ increased with increasing oxygen content as well as E$_{opt}$ at the same B$_2$H$_6$ gas ratio in the p-tpye a-SiO$_x$:H [8]. However, our deposition condition of gas ratio is a variable factor for both the N$_2$O and B$_2$H$_6$ gas ratio. For this case, the absorption in the defect region increased with increasing the N$_2$O and B$_2$H$_6$ gas ratio. Therefore the value of N$_D$ is highest at the condition regarding N$_2$O of 50% and the B$_2$H$_6$ 1% gas ratio. Therefore, the variation of these gas ratios will be acting as dopants for the role of increasing conductivity, E$_{opt}$ and defect.

Figure 3 contains the room-temperature dark conductivity (σ$_d$), photo conductivity (σ$_{ph}$) [(a)] and activation energy [(b), derived from the temperature dependence of σ$_d$] for p-type a-SiO$_x$:H films as a function of oxygen content. It provides a correlation between the effect of dopant-B$_2$H$_6$ and oxygen and conductivity. The value of σ$_d$ and σ$_{ph}$ increased with increasing the B$_2$H$_6$ ratio at the same oxygen ratio. The value of σ$_d$ and σ$_{ph}$ also increased with the rising N$_2$O ratio at the same B$_2$H$_6$ ratio. The p-type a-SiO$_x$:H film with N$_2$O 50% and B$_2$H$_6$ 1% has σ$_d$ and σ$_{ph}$ of 9.79×10^{-7} S/cm and 1.71×10^{-6} S/cm. From the conductivity between the variable B$_2$H$_6$ and the N$_2$O ratio, we can deduce that the B$_2$H$_6$ ratio is a superior factor. One possible reason for this may be that boron doping can compensate the donor like states created by oxygen in boron doped a-SiO$_x$ films [8]. As the oxygen atoms with three fold coordination have extra electrons so the oxygen-induced donor like states move the Fermi-level causing the increase of σ$_d$ and σ$_{ph}$. The activation energy is the energy distance between EF and the valence band edges as shown in Fig. 3(b). The activation energy is 0.49-0.57 eV for the p-type a-SiO$_x$:H films with E$_{opt}$=2.03~1.91 eV. The activation energy increases with the in-

crease of B$_2$H$_6$ and N$_2$O ratios. The shifting of Fermi level towards the valence band due to the incorporation of oxygen and boron may be the reason for the increase of activation energy [9,10].

Figure 4 shows the refractive index and E$_{opt}$ of p-type a-SiO$_x$:H films as a function of photon energy with different B$_2$H$_6$ ratios and N$_2$O ratios. The E$_g$ slightly increased from 1.91 to 2.03 eV with increasing oxygen content. The oxygen corporation replaced Si-Si bonds with Si-O-Si bonds in the films [11]. The Si-O-Si bridge has a stronger bond energy compared to the Si-Si bond energy due to either a decrease in the band width or an increase in the energy difference between bonding and anti-bonding splitting regarding Si-Si derived bonds [12]. The bond energies for the Si-O bond in SiO$_2$ and the Si-Si bond in c-Si appears to be 4.8 eV and 2.3 eV, respectively [13]. The B$_2$H$_6$ often attributed to the increase of disorder in the network and the removal of oxygen from the p-type a-SiO$_x$:H films. Therefore, the intensity of Si-O peak decreases as a consequence of oxygen removal from the growing precursors with increasing B$_2$H$_6$ ratio. As a result the E$_{opt}$ decreased with the increase of the B$_2$H$_6$ ratio. Figure 4 also represents the variation of the refractive index (n) with different oxygen content. The refractive index is expected to depend on the density of films and their electronic band structure [10]. We also observed that the refractive index decreases from 3.62 to 3.18 at the beginning of O-incorporation into the p-type a-SiO$_x$:H film network. The decrease in regards to the refractive index may be due to an increase of voids and disorder in films through the incorporation of oxygen [14].

For the high conversion efficiency of a-Si solar cells, the p-layer should have high E$_{opt}$, low E$_a$, high conductivity, and low absorption. We further apply p-type a-SiO$_x$:H films (N$_2$O 30% and

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B_2H_6 0.5%) and (N_2O 30% and B_2H_6 1%) to a-Si solar cells.

Figure 5 shows the current - voltage (I-V) characteristics of the a-Si solar cells with 0.5 and 1% of B_2H_6 ratios. The cells with V_{oc} = 0.853 and 0.842 V, J_{sc} = 13.87 and 15.13 mA/cm², fill factor = 0.664 and 0.656 and a conversion efficiency of 7.54 and 8.36% have been obtained. The V_{oc} and FF slightly decreased while J_{sc} increases with higher a B_2H_6 ratio. The higher E_{opt} of the B_2H_6 0.5% condition compared to the B_2H_6 1% condition will result in a higher V_{oc}. The higher E_{opt} has a higher built-in potential energy in the solar cell. The lower J_{sc} and a higher FF coincides with the tendency of theoretical efficiency limits for homojunction solar cells [15].

The quantum efficiency of a-Si solar cells for different p-type window materials is presented in Fig. 6. We used three different devices with the following (p-type a-SiO$_x$:H with E_{opt} of 1.75 eV), (a-SiO$_x$:H(p) with E_{opt} of 1.94eV) and (p-type a-SiO$_x$:H with E_{opt} of 1.91 eV) conditions. The effect of E_{opt} has been represented in the short wavelength region and by increasing E_{opt}, whereby the intensities of the spectral response increases.

4. CONCLUSIONS

We prepared p-type a-SiO$_x$:H films by optimizing the optical bandgap, electrical conductivity, and activation energy with the PECVD process of SiH_4, H_2, N_2O and the B_2H_6 gas mixture. The E_{opt} was found to increase with an increase of the N_2O gas ratio through the incorporation of oxygen but decreased with an increase of the B_2H_6 ratio. There is an increase in σ_d, σ_{ph} and Ea with increasing both the B_2H_6 and N_2O ratio. Here, we selected two p-type a-SiO$_x$:H films with good optical bandgap, dark conductivity and activation energy for the applications regarding a-Si solar cells. We employed these two p-type a-SiO$_x$:H films for the a-Si silicon solar cell. The increase in J_{sc} of the device with B_2H_6 (1%) as compared to B_2H_6 (0.5%) was related to E_{opt}. A conversion efficiency of 7.54 and 8.56% at the B_2H_6 (0.5 and 1%) ratio was achieved demonstrating the effectiveness of the silicon oxide (SiO$_x$) material.

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